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(57) Abstract

Waterless and wet lithographic plates precursors are prepared as composites comprising presensitized (PS) lithographic plate precursors supporting radiation-ablative coatings containing an ablation sensitizer and an imaging amount of a non-ablative ultra-violet (UV) absorber. Digitized IR laser image inscription within the ablative coatings initiates ablation-driven transfer of the UV absorber to the PS plate. UV exposure of the plate followed by conventional development provides lithographic plates that exhibit high impression life suitable for high volume printing runs.

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THERMAL ABLATION TRANSFER LITHOGRAPHIC PRINTING PLATES

Field of the Invention

The present invention relates to novel ablation-transfer imaging lithographic plate precursors and to the digitized infra-red (IR) laser imaging process employed therewith. The invention particularly relates to composites comprising presensitized (PS) lithographic plate precursors supporting IR radiation-ablative coatings or films containing an ablation sensitizer and an opacifying amount of a non-ablation ultra-violet (UV) absorber. The coating or film is in essentially coextensive contact with or deposited upon a film that is transparent to an IR Laser. The imaging method involves digitized image inscription within the radiation-ablative coatings or film by an IR laser to initiate ablation-driven transfer of the UV absorber composition to the PS plate. Subsequent overall exposure of the plate to UV light followed by conventional development of the exposed PS plate provides lithographic plates suitable for high volume printing runs.

Background of the Invention

Laser-induced ablation-transfer imaging (TAT) is well known for applications such as color proofing, security coding and the production of masks for the graphic arts field and printed circuitry. Laser-induced ablation-transfer imaging is thought to be effected by the rapid and transient accumulation of pressure beneath and/or within a mass transfer layer initiated by imagewise irradiation. Transient pressure accumulation can be attributed to one or more of the following factors: rapid gas formation via chemical decomposition and/or rapid heating of trapped gases, evaporation, photo and thermal expansion, ionization and/or by propagation of a shockwave. The force produced by the release of such pressure is preferably sufficient to cause transfer of

the imaging layer to an adjacent receptor element.

Laser heating has been employed in the art in lieu of known methods such as the use of thermal printing heads. In these systems, the donor sheet includes a material which strongly absorbs at the wavelength of the laser emission. In the thermal melt transfer process, when the donor sheet is irradiated the absorbing material converts the laser light to thermal energy and transfers the heat to a colorant transfer layer which also includes a binder, fusible compound, etc., thereby raising its temperature above its melting point to effect its transfer onto an adjacent receptor sheet.

Thermal ablation transfer donor media have been described in the art (US 5,156,938/ US 5,171,650/ US 5,256,506/ US 5,326,619 and WO 95/05623) and used in numerous applications such as color proofing, security coding, production of mask for the graphic arts and printed circuits.

U. S. patent 5,156,938 teaches an ablation-transfer imaging medium comprising a support substrate and a laser-ablative topcoat having a non-imaging ablation sensitizer and an imaging amount of a non-ablation sensitizer contrast imaging material contained therein.

PCT patent WO93/12939 teaches donor elements for laser-induced thermal imaging processes comprising a support bearing thereon a colorant layer comprising a colorant and a selected infrared absorbing layer azamethine compound.

U. S. patent 5,256,622 teaches a dye-donor element for use with laser-induced thermal transfer wherein the dye layer comprises a dye dispersed in a polymeric binder and wherein the binder has an intrinsic viscosity of at least 1.6.

While it is known that the thermal ablation transfer media can also be used for direct computer-to-plate application, the materials of the image area that transfer from the donor layer to the aluminum substrate are usually low molecular weight and are partially decomposed by heat during the laser imaging. Furthermore, adhesion of the donor element to the aluminum substrate or to protective film layer has persistently been poor. This results in printing plates that do not have a long impression life due to poor mechanical properties and adhesion. The problem severely limits the applicability of laser-induced thermal ablation transfer as a method for imaging lithographic plates. This invention is immediately directed to a resolution of the problem and describes the composition and method for thermal ablation transfer laser imaging of PS lithographic printing plates having a long impression life.

In addition to resolving the problem of extending the usefulness of TAT lithographic plates to high production runs of commercial printing applications, it would be a major contribution to the Graphic Arts industry if the advantages of laser-induced ablation-transfer imaging could be applied to the production of waterless lithographic plates.

In conventional planographic printing, a printing plate bearing an oleophilic, ink receptive image is dampened with an aqueous fountain solution to prevent ink from wetting the hydrophilic, non-image bearing areas of the printing plate, after which an oil-based ink is rolled over the plate to selectively coat the now printable image. These are known herein as wet plates. Conventional planographic printing has some difficulties inherent in having both an oleophilic ink and an aqueous fountain solution conjoined in the same press. First, the fountain solution applied to the printing plate flows back into the train of inking rollers on the press,

causing emulsification of the ink. Secondly, it is difficult to maintain control of the delicate balance needed between the amount of ink and the amount of fountain solution applied to the printing plate. Consequently, the image fidelity and uniformity are difficult to maintain. Thirdly, the fountain solution tends to flow forward over the offset cylinder, moistening the copy paper and thereby causing its dimensional change. Fourthly, in the case where printing is imaged directly by electrophotography, the imaged printing plate must be subjected to an etching treatment and the printing operation becomes complicated.

Considerable effort has been applied in the industry directed toward the development of lithographic printing plates that may overcome some of the foregoing problems. A significant portion of that effort has been directed toward the development of planographic plates that do not need a fountain solution circulating in the printing apparatus to accomplish the printing function. These plates are referred to herein as waterless plates or dry plates. For these waterless plates, the circulating fountain solution is avoided by the discovery of various printing methods and plate/ink compositions that do not rely on the induced hydrophilicity of a portion of the plate to distinguish an oleophilic image surface from a non-oleophilic non-image surface.

US patent 4,259,905 teaches a waterless, contact speed planographic printing plate having an overlaying modified organopolysiloxane polymeric material layer. The plate exhibits enhanced printing endurance and produces prints of low background contamination.

US patent 4,342,820 teaches a negative working waterless plate requiring no dampening water for use in negative work which comprises a base substrate, a light releasing photosensitive layer overlaying the base

substrate and the silicone rubber layer overlaying the photosensitive layer. When the printing master plate is exposed through a negative film and then treated with a developer, only the silicone rubber layer overlaying the exposed photosensitive layer is removed, while the photosensitive layer remains as it is to form an image area. Dampening water is not required when printing is carried out.

US patent 3,894,873 teaches a positive working waterless plate, comprises a base substrate, a light sensitive photoadhesive layer overlaying a base substrate and the silicone rubber layer overlaying the photoadhesive layer. When the printing master plate is exposed through a positive transparency and then treated with a developer, only the silicone rubber layer overlaying the unexposed photoadhesive layer is removed, while the photoadhesive layer remains as it is form an image area.

The waterless plates described in the foregoing patents are of contact speed and do not use the TAT process. The term "contact speed" means that a light-sensitive material has a sensitivity such that it can be exposed through a negative or positive transparency placed in contact with it.

A principal objective of the present invention is to provide an imaging process for lithographic plate precursors employing digitized, laser-induced thermal ablative transfer that yields a plate having high impression life of at least 50,000 copies, preferably at least 100,000 copies.

Another objective is to provide a donor element composition with the adhesive strength and donor element qualities needed to support the desired impression life.

Yet another objective is to provide plate and donor element compositions that can be used to produce waterless as well as wet lithographic plates.

Summary of the Invention

The aforestated problem and challenges of preparing wet and waterless lithographic printing plates by thermal ablation transfer wherein the plates produced have a long impression life has been overcome by the discoveries inherent in the instant invention. These discoveries include the use of presensitized lithographic plate precursor composites coated with at least one donor layer containing a composition of UV and IR dyes and absorbers that facilitate the formation of an image-mask on the presensitizing coating layer of the plate. The image-mask is transferred to the PS coating during IR irradiation of the composite. Development of the PS layer with conventional PS plate developers removes the mask and non-image area and produces the desired high impression life lithographic plate. By utilizing the compositions and imaging process described herein, wet and waterless lithographic printing plates can be prepared by thermal ablation transfer.

A further element of the innovations of the instant invention is in the variations which can be used for the donor layer compositions. The donor layer compositions can be altered to provide laser imagable wet and waterless lithographic plate precursors. In a wet plate the donor layer is soluble in water and can be removed during processing of the plate; in a waterless plate the donor layer is soluble in non-aqueous organic solvents.

More particularly, a digitized, infra-red laser-induced imaging method for presensitized lithographic plate precursors having at least a coating layer containing a UV-opaque, thermal transfer donor-element has been discovered. The method comprises imagewise

exposure or inscription of the plate with the laser. The plate precursor contains a first presensitizing coating layer, a second layer comprising said donor-element coating and a third IR transparent film layer. Those portions of the second and third layers unexposed to IR laser are removed. The treated plate is then exposed overall to ultraviolet light. For positive plates, the PS layer is developed in an aqueous developer solution to remove those portions of the presensitizing coating exposed to UV light. The method yields an image-bearing lithographic printing plate suitable for high production printing runs or impression life.

The presensitized plate precursor of the invention may further contain an intermediate UV transparent film layer between the first PS layer and the second or donor element containing layer. After exposing the treated plate overall to UV light, the intermediate layer is removed, preferably by dissolving in aqueous developers. For waterless plates, the intermediate layer can be removed mechanically such as by peeling, .

The composition of the wet plate of the invention comprises a digitally controlled laser imagable lithographic printing plate precursor comprising a supporting substrate such as aluminum; a first layer on the substrate comprising a positive-working or negative-working coating; a second layer comprising a thermal transfer donor-element coating; and a third IR transparent film layer. Optionally, the composition may include a UV transparent film between the first and second layers.

For positive plates, the waterless plate of the invention specifically comprises a hydrophilic or non-hydrophilic solid substrate; a first layer on the substrate comprising an oleophilic coating; a second layer comprising a positive working photoadhesive coating

containing quinonediazides having solubilizable properties upon exposure to actinic light; an actinic light transparent third layer comprising a solvent swellable, ink repellant silicone rubber; a fourth layer comprising a polymeric film that is transparent to ultraviolet light; a fifth layer comprising the donor-element coating and a sixth IR transparent polymeric film layer.

The thermal transfer donor layer of the invention comprises either non-aqueous organic solvent soluble components including binder resins, waxy tackifiers, UV-dyes, infrared dyes and UV-absorbers or water soluble components including binder resins, waxy tackifiers, UV-dyes, infrared dyes and UV-absorbers.

Description of the Figures

Figure 1 illustrates the structure and image processing steps of a wet plate of the invention.

Figure 2 illustrates the structure and image processing steps of a waterless plate of the invention.

Detailed Description of the Invention

In the instant invention ablation-transfer imaging lithographic plate precursors are prepared and used with digitized infra-red (IR) laser imaging processes. Both waterless and wet lithographic plate precursors are prepared as composites comprising at least presensitized (PS) lithographic plate precursors supporting radiation-ablative coatings or films containing an ablation sensitizer and an opacifying amount of a non-ablative ultra-violet (UV) absorber.

The PS plate precursors of the invention are described as containing positive-working or negative working coatings. However, this terminology is borrowed for communication convenience from well-known conventional lithographic plate making art which uses

positive and negative film (hence positive-working and negative-working PS coatings) in a photographic process to produce a printable image on the plate. The present invention does not employ a photographic process; nor are positive or negative films used in any part of the process. However, digital information may be described as positive or negative. Furthermore, although the wet plate precursors of the invention employ conventional positive-working and negative-working coating chemistry well known in the art for PS coating formation, there is a role reversal for waterless plates. For waterless plates, conventional wet plate positive-working coating chemistry known in the art is used to produce waterless plates commonly referred to as negative-working and conventional wet plate negative-working coating chemistry known in the art is used to produce waterless plates commonly referred to as positive-working.

Referring to the Figures, Figure 1 describes the wet or conventional lithographic printing plate of the invention. The plate comprises a thermal transfer donor layer [104] coating on and below a laser transparent plastic support [105]; a photosensitive receiving layer [102] coating an aluminum substrate [101] and an optional intermediate water soluble layer separating the donor and receiving layers [103].

Referring to Figure 2, the negative-working waterless lithographic printing plate of the invention is described. The plate comprises a substrate [201], preferably aluminum; a first layer [202] comprising an oleophilic prime coating, preferably an epoxy or polyurethane coating; a second layer [203] comprising a UV light sensitive PS coating; a third layer [204] comprising a solvent swellable, ink repellent silicone rubber coating; a fourth layer [205] comprising a polymeric film, preferably polyolefin, which is transparent to UV light and electrostatically adhered to

the silicone layer; a fifth layer comprising an IR sensitive thermal transfer donor layer [206] coating;and a sixth layer [207] comprising an IR laser transparent protective plastic film, preferably Mylar.

The imaging process for the wet plate and waterless plate of the invention are similar. For the wet plate as shown in Figure 1, the process comprises the following steps: (i) imaging the plate by infrared laser [106] having a wavelength between 800 and 1300 nm; (ii) removal of the thermal transfer donor film and the transparent plastic support by peeling [107]; (iii) exposure of the plate overall under UV-light [108]; and (iv) chemical development to obtain the final printing image [109].

For the waterless plate as shown in Figure 2, the process is similar to that of the wet plate except that the transferred image is removed by peeling off the polyolefin film, i.e., layer [205]. The silicone rubber layer is removed by soaking or brushing with a developer as described in U. S. Patents 4,342,820, 4,259,905, 3,894,873 and U. S. Patent 5,512,420. These patents are incorporated herein by reference. The patents describe the application and development of both negative-working and positive-working waterless lithographic plates.

The following Examples illustrate the preparation of the conventional, i.e., wet, and the waterless plates of the invention:

Examples 1-5

Preparation and Imaging of Waterless Thermal Ablation Transfer (TAT) Lithographic Plates

The organic washable thermal ablation transfer donor layer was prepared by dissolving binder resins, waxy tackifiers, UV-dyes, infrared dyes, UV-absorber (see

Table 1) in 100 grams solvent mixture which contains 59.5% methyl ethyl ketone, 19.4% methyl cellosolve, 119.4% methanol and 0.2% Fluorad 430 surfactant. The solutions were filtered to remove the solid residues and then coated on Mylar film (thickness between 0.1 and 0.5 mil) by using a wire-wound rod to produce a uniform coating having an optical density of 2.5. The thermal ablation transfer donor film was then laminated in face-to-face contact onto the waterless lithographic printing plates which are currently marketed by Polychrome Corp. as positive Toray and negative Toray waterless plates.

The image was inscribed on the TAT-plate by using a 830 nm infrared lasers at an energy between 100 and 500 mJ/cm^2. The thermal ablation film was peeled off to obtain a uniform and high resolution image which transferred to the photosensitive receiving layer. The plates were exposed under UV-light between 100 and 500 mJ/cm^2. The polyolefin film was peeled off and the exposed plates were subjected to chemical development with appropriate hydrocarbon developers as described hereinafter to produce a clean printing image.

Table I

Waterless Plate Coating Compositions of the Organic Soluble Thermal Transfer Donor Layer

Ingredients	Suppliers	Examples (gram) 1	2	3	4	5
Binder resins						
Ethyl cellulose	Hercules	1.0	---	---	---	1.0
Hydroxypropyl cellulose	Hercules	---	1.0	---	---	---
Nitrocellulose	Hercules	---	---	1.0	---	---
Acrylic resin A-21	Acryloid	---	---	---	1.0	---
Wax tackifiers						
Sylvatac 295 rosin	Arizona Chemical	1.0	1.0	1.0	1.0	1.0
UV-Dyes and absorbers						
Spirit nigrosine	Dye Specialties	1.0	1.0	1.0	1.0	1.0
Black dye	BASF	0.5	0.5	0.5	0.5	0.5
Infrared dyes and pigments						
Cyasorb IR99	GPT	1.0	1.0	1.0	1.0	---
Carbon black FW18	Degussa	---	---	---	---	1.0

Table 2

Wet Plate Compositions of the Water Soluble Thermal Transfer Donor Layer.

Ingredients	Suppliers	Examples (grams) 6	7	8	9	10
Binder resins						
Polyvinyl alcohol (Airvol 523)	Air Products	1.0	---	---	1.0	---
Polyvinyl pyrrolidone K90	GAF	---	1.0	---	---	1.0
Polyethylene oxide	Aldrich	---	---	1.0	---	---
Waxy Tackifiers						
Polyethylene glycol	Aldrich	1.0	1.0	1.0	---	---
Lanolin	Arizona Chemical	---	---	---	1.0	---
UV dyes and absorbers						
Nigrosine WSY	Dye Specialties	1.0	1.0	1.0	1.0	---
Spectramine Black	Spectra Color	0.5	0.5	0.5	0.5	---
Infrared dyes and pigments						
PINA 780	Hoestch	1.0	1.0	1.0	1.0	1.0
Carbon black FW18	Degussa	---	---	---	---	---

Example 6 - 10 (Table 2)
Preparation and Imaging of Conventional (Wet) Thermal Ablation Transfer Lithographic Plates

The water washable thermal ablation transfer donor layer was prepared by dissolving water soluble binder resins, waxy tackifiers, UV-dyes, UV-absorbers, infrared dyes (see Table 2) in 100 grams of aqueous solution containing 10% 2-methyl-1-pyrrolidone, 10% methanol and 1% surfanol TG surfactant. The solution was filtered to remove the solid residue and coated on the Mylar film by using a wire-wound rod to produce a uniform coating having optical density between 2.5 and 3.0. The thermal ablation transfer film was laminated in face-to-face onto the positive lithographic printing plates which are currently marketed by Polychrome as T-41, X-60, Virage, Vista 360, XLR, Vista-M and HSP.

The image processing of the obtained wet plates was carried out in a manner similar to that described in Examples 1 to 5 except for development of the waterless plate silicone rubber layer of Examples 1-5. The imaging and development process for the wet plates of the invention is described hereinafter. Developers useful for wet plates are available from Polychrome Corp. and include PC900, PC955, PC952, PC3000 and PC3500.

I. Waterless and Wet Lithographic Plate Composition

The lithographic printing plate precursor of the invention is constructed of a substrate with four layers deposited on the substrate.

The Substrate Layer

The substrates which can be used in the instant invention for waterless or wet printing applications are those having the mechanical strength needed to withstand the rigors of the printing process in which it is used. Solid substrates can be manufactured from metal, wood,

film, or composite material. When the printing process in which the plate is used is a waterless process, the substrate is not restricted to those having a hydrophilic surface as conventionally practiced. The substrate useful in the invention can have either a hydrophilic, ink-repellent surface for wet printing or hydrophobic surface for waterless printing as long as the surface can be adapted to retain the first, presensitized coating layer. An aluminum substrate is preferred in view of its mechanical strength and the familiarity of that substrate to the printing industry.

The Prime Coating (Waterless Plate)

For waterless plate applications, the substrate is coated with a prime coating that comprises an oleophilic, flexible, ink receptive layer. Any oleophilic coating ean be used; however, preferred coating are epoxy coatings and polyurethane coatings. Other useful coatings include phenolics, polyesters, polystyrene and polyacetates.

The Photosensitive Layer

The PS layer of the plate may be a conventional positive-working photosensitive layer or alternatively a conventional negative-working photosensitive layer. In either case, the primary attributes of the negative or positive working coating of the first layer are sensitivity toward chemical conversion upon exposure to actinic light and a capability to act as an adhesive bonding agent with the second or overlying silicone rubber layer of waterless plates.

i. negative-working photosensitive layer

The photosensitive layer for a negative-working presensitized plate of the invention comprises an ethylenically unsaturated photopolymerizable monomer or oligomer having a boiling point above 100°C derived from alcohols or amines having less than 30 carbon atoms or

polyalcohols or polyamines having less than 80 carbon atoms, a photoinitiator and, if necessary, an inhibitor of heat polymerization, polymeric materials or an inorganic powder. Examples of useful coatings are listed in US Patent 3,894,873 and are provide by Polychrome Corporation as Vista 360, XLR, Vista M or HSP plates. The unsaturated monomers or oligomers are acrylates or methacrylates such as dimethylaminoethyl methacrylate, polyethylene glycol dimethacrylate, 3-chloro-2-hydroxypropyl methacrylate, N,N,N',N' tertrakis-2-hydroxy-3-methacryloyloxy propylxylylenediamine, hydroxyacetoneacrylamide, or N-methoxymethylacrylamide.

Examples of photoinitiators include benzophenone, Michler's ketone, xanthone, benzoin, benzoin methyl ether, benzoin isopropyl ether, dibenzyl disulfide and uranyl nitrate.

Examples of polymeric materials include unsaturated polyester resins composed of units selected from ethylene oxide, propylene oxide, phthalic acid, bisphenol-A, maleic anhydride and fumaric acid, polyvinyl acetate, polybutylmethacrylate, polyoctylmethacrylate, polyethylene oxide, and soluble nylon copolymers.

In order to maintain photosensitivity of the presensitized plate and prolong the storable period very small amounts of heat polymerization inhibitor are preferably added to the photoadhesive layer composition. Examples of such inhibitors are hydroquinone, methyl ethyl hydroquinone, phenothiazine, 2,4-dinitrophenol and triphenylmethane.

If necessary, other additives may be included in the photoadhesive layer to make it solid enough to support the silicone rubber overlayer parallel with the base layer. The resulting plate shows a high scratch resistance and excellent storability.

ii. Positive-working photosensitive layer

The alternative positive-working photosensitive, layer of the presensitized plate of the invention comprises the quinonediazides usually employed for conventional positive working presensitized plates in the lithography plate manufacturing art, wipe-on plates or photoresist. These include the ester obtained from benzoquinone-1,2-diazide sulfonates or naphthoquinone-1,2-diazide sulfonates and polyhydroxy compounds, e.g. benzoquinone-1,2-diazide sulfochloride with polyhydroxy phenyl, the ester from naphthoquinone-1,2-diazide sulfochloride and pyrogallol acetone resin, the ester from naphthoquinone-1,2-diazide sulfochloride and phenol-formaldehyde novolak resin; or complexes of diazonium compounds and inorganic or organic acids, e.g., a photosensitive complex of diazodiphenylamine and phosphotungstic acid. The preferred components are selected from the group consisting of a reaction product of a quinonediazide with a polyfunctional compound, quinonediazide urethanized with a monoisocyanate, an esterified quinonediazide, an amidized quinonediazide, a quinonediazide graft polymerized with a vinyl monomer, so that the photosensitive layer is substantially insoluble in a developer. Useful positive-working plates are available from Polychrome Corporation as T-41, X60 and Virage.

The polyfunctional compounds employed as crosslinking agents are polyisocyanate compounds, e.g., paraphenylene diisocyanate, 2,4 or 2,6-toluene diisocyanate, 4,4′-diphenylmethane diisocynate, hexamethylene diisocyanate, isophorone diisocyanate, or adducts thereof, and polyepoxy compounds. e.g. polyethylene glycol diglycidyl ethers, polypropylene glycol diglycidyl ethers, bisphenol A diglycidyl ether, and trimethylolpropane triglycidyl ether. It is necessary that the curing operation with these crosslinking agents

be carried out under conditions under which the photosensitive substance will not lose its photosensitivity, usually at a temperature not higher than 126°C . A catalyst may be added if necessary. The most preferred composition is a condensation product of quinonediazide naphthoquinone-1,2-diazide-sulfonate with phenol-formaldehyde novolak resin. Examples of useful coatings are listed in US patent 4,342,820.

Silicone Rubber layer (Waterless Plates)

The silicone rubber layer of this invention comprises crosslinked diorganosiloxane obtained by curing silicone gums. Essentially, they are elastomers of high-molecular weight of about 400,000 to 800,000 formed by crosslinked linear diorganopolysiloxanes, preferably dimethylsiloxane. Silicone rubbers suitable for use in the present invention are well known and are listed in US patents 3,894,873 and 4,342,820.

For waterless plates, the positive photosensitive layer is capable of releasing the silicone rubber layer and constituting an image area in a selected area to be exposed to the actinic light so that the silicone rubber layer can be removed in the exposed image by a developer.

The Film Layer

The film layer of the plate of the invention may optionally be a film that is transparent to UV light when a wet plate is prepared. Preferred films for the wet plate include PVA and polyvinylpyrrolidone. For waterless plates, a UV light transparent film is also used, but the preferred films are polyolefins, especially polypropylene. Other useful films include polyethylene, polyesters such as Mylar, cellulose acetate, polyimides and polyvinyl acetate. The films may be treated by methods such as corona discharge to promote electrostatic bonding of the film to the silicone rubber layer of the waterless plate

The Donor Element Layer

For the wet plate, the donor element layer is composed of aqueous or aqueous alkali soluble binder resins, waxy tackifiers, UV-dyes, infrared dyes and UV absorbers. For waterless plates, organic solvent soluble resins, tackifiers, UV-dyes, infrared dyes and UV absorbers are used.

Useful water soluble resins include polyvinyl alcohol, polyvinylpyrrolidone and polyacrylic acids.

Useful organic soluble resin binders include polymethylmethacrylate, polycarbonate, polyvinylpyrrolidone and nitrocellulose.

Useful UV dyes include those having a maximum wave length between 300 and 500 nm and include Nigro fine, Victoria Blue and Disperse dyes.

Useful IR dyes for the plate precursors of the invention include cyanine dyes, phthalocine dyes and Sgnaraine dyes.

The Top IR transparent Film Layer

The transparent film may be thinner than 10 mils (preferably thinner than 4 mils) to obtain good image fidelity. However, the film should be capable of providing an effective barrier to atmospheric oxygen in order to protect the reactivity of the intermediate layers. Representative examples of such a transparent film include polyethylene, polypropylene, polyvinyl chloride, polyvinyl acetate, polyvinyl alcohol, polystyrene, polyethylene terephthalate, polycarbonate, cellulose triacetate, polyester (Mylar by Dupont) etc.

In the present invention the preferred transparent films are polyolefin films such as polyethylene and polypropylene which have been treated to enhance their

ability to adhesively bond with other films. However, an overriding characteristic of the preferred films and any film used is transparency to infra-red light in the wavelength transmitted by the imaging IR laser.

II. Detailed Description of The Imaging Process

In the instant invention a digitally controlled laser is a preferred method for imagewise treatment of the plate to form an image in the donor layer and transfer that image as a mask to the subordinate layer of the plate. It is known that photographic processes of making positive and negative film originals is time consuming and causes uncontrolled variations in the process. Facilities and equipment adequate to support the process are required. To avoid these limitations, electronic alternatives adaptable to plate imaging have been developed that result in better control of plate making, including digital direct plate making systems and especially systems coupled to laser imaging devices. For digital plate making, the textual and graphics information stored in desk top publishing or digital data storage systems can be modified on the computer before digitizing onto the plate. The high speed of text printing from the resultant digitized plate provides considerable productivity improvements over the conventional mode of platemaking. Hence, in the present invention digitally controlled image production is preferred using a laser beam.

The method for image production on waterless lithographic printing plates using the photosensitive lithographic printing plate precursor of the present invention is depicted in the following steps:

o inscribing a masking image in the donor element layer using an IR laser at an energy level of between 100 and 500 mJ/cm^2;

o peeling away the Mylar top layer and the attached unexposed portion of the donor element layer;

○ exposing the plate overall to UV light at between 100 and 500 mJ/cm^2;

○ removing the polyolefin film layer and the attached imaging mask by peeling to reveal the UV exposed and unexposed portions of the silicone rubber layer;

○ developing the silicone rubber layer using known solvents to remove the unexposed portion of silicone;

○ developing the now revealed unexposed portions of the PS layer to provide an oleophilic image.

The developing liquids for positive working waterless plate are those which can be absorbed by the cured silicone rubber and swell the said layer without affecting or weakening the bonding of the photosensitive layer to the silicone rubber in the image area. The most useful developing liquids include isoparaffin or linear hydrocarbon, or a mixture having those major components. These liquids are commercially and economically available from the fractional distillation products of petroleum. The fractions having lower boiling point are more absorbed by the silicone rubber, which is more swollen and consequently can be removed more easily then those treated by the fraction of higher boiling point. Thus gasoline is one of the most useful, convenient and economical developing liquids. These hydrocarbons do not usually affect and dissolve even the unhardened photoadhesive layer which remains on the plate surface after the removal of the silicone rubber layer in the image area.

Developing liquids for negative working waterless plate are those which are capable of swelling silicone rubber. These are aliphatic hydrocarbons (e.g. hexane, heptane, gasoline, kerosene), aromatic hydrocarbons (e.g. toluene, xylene), or halogenated hydrocarbons (e.g. trichloroethane) and the following polar solvents : alcohols (e.g. methanol, ethanol), ethers (e.g. ethyl cellosolve, dioxane; ketones (e.g. acetone, methyl ethyl

ketone; esters (e.g. ethyl acetate, cellosolve acetate).

The method for image production on wet lithographic printing plates using the photosensitive lithographic printing plate precursor of the present invention is depicted in the following steps:

○ inscribing a masking image in the donor element layer using an IR laser at an energy level of between 100 and 500 mJ/cm^2;

○ peeling away the Mylar top layer and the attached unexposed portion of the donor element layer;

○ exposing the plate overall to UV light at between 100 and 500 mJ/cm^2;

○ developing the image to remove the attached imaging mask and the unexposed portion of the PS layer using conventional aqueous developing agents.

What is claimed is:

1. An infra-red laser-induced imaging method for multilayed presensitized lithographic plate precursor(s), said method comprising:

i. inscribing an image upon said plate with said laser wherein said plate comprises a substrate, a first presensitized positive-working or negative-working coating layer on said substrate, a second layer comprising a UV-opaque, thermal ablation transfer donor-element, and a third IR transparent film layer;

ii. treating said inscribed plate to remove that portion of said second and third layers unexposed to said IR laser;

iii. exposing said treated plate overall to ultraviolet light; and

iv. image-wise developing said first layer.

2. The method of claim 1 wherein said presensitized plate further contains an intermediate UV transparent film layer between said first and second layer, wherein said intermediate layer is removed after exposing said treated plate overall to UV light.

3. The method of claim 2 wherein said presensitized plates comprise positive-working presensitized plates.

4. The method of claim 1 wherein said presensitized plates comprise negative-working presensitized plates.

5. The method of claim 1 wherein said donor-element comprises organic solvent soluble binder resins, waxy tackifiers, UV-dyes, infrared dyes and UV-absorbers soluble.

6. The method of claim 1 wherein said image is inscribed by a digitally controlled IR laser.

7. An infra-red laser imagable lithographic printing plate precursor comprising:

a supporting substrate;

a first layer on said substrate comprising a positive-working or negative-working coating;

a second layer comprising a thermal ablative transfer donor-element coating; and

a third IR transparent film layer.

8. The plate of claim 7 further containing an intermediate UV transparent film layer between said first and second layer.

9. The plate of claim 7 wherein said donor-element comprises water or aqueous alkali soluble binder resins, waxy tackifiers, UV-dyes, infra-red dyes and UV-absorbers.

10. The method of claim wherein said plate comprises a waterless plate comprising a supporting substrate, a first oleophilic coating on said substrate, a second presensitizing positive-working or negative-working coating layer, a third layer comprising a silicone rubber coating, a fourth layer comprising a UV transparent film, a fifth layer comprising said donor-element coating and a sixth layer comprising said IR transparent film; wherein said method further includes the steps of:

i. removing the sixth layer and that portion of the fifth layer unexposed to the IR laser;

ii. exposing said plate overall to ultraviolet light;

iii. removing said UV transparent film;

V. developing the silicone rubber layer to remove the unexposed portion of said silicone.

11. The method of claim 10 wherein said donor element comprises organic solvent soluble binder resins,

waxy tackifiers, UV-dyes, infrared dyes and UV-absorbers soluble.

12. The method of claim 10 wherein said UV transparent film is selected from the group comprising polyolefin film, cellulose acetate, polyester, polyimidies, and polyvinyl acetate. and said IR transparent film comprises polyester film.

13. The method of claim 10 wherein said UV transparent film comprises polypropylene.

14. The method of claim 10 wherein said IR transparent film comprises polyester film.

15. The method of claim 10 wherein said oleophilic coating comprises an epoxy coating or polyurethane coating.

16. An infra-red laser imagable waterless lithographic printing plate precursor comprising:

a supporting substrate;

a first layer on said substrate comprising an oleophilic coating;

a second presensitizing positive-working or negative-working coating layer;

a third layer comprising a silicone rubber coating;

a fourth layer comprising a UV transparent film;

a fifth layer comprising a thermal ablative transfer donor-element coating; and

a sixth layer comprising an IR transparent film.

17. The plate of claim 16 wherein said donor-element comprises organic solvent soluble binder resins, waxy tackifiers, UV-dyes, infrared dyes and UV-absorbers.

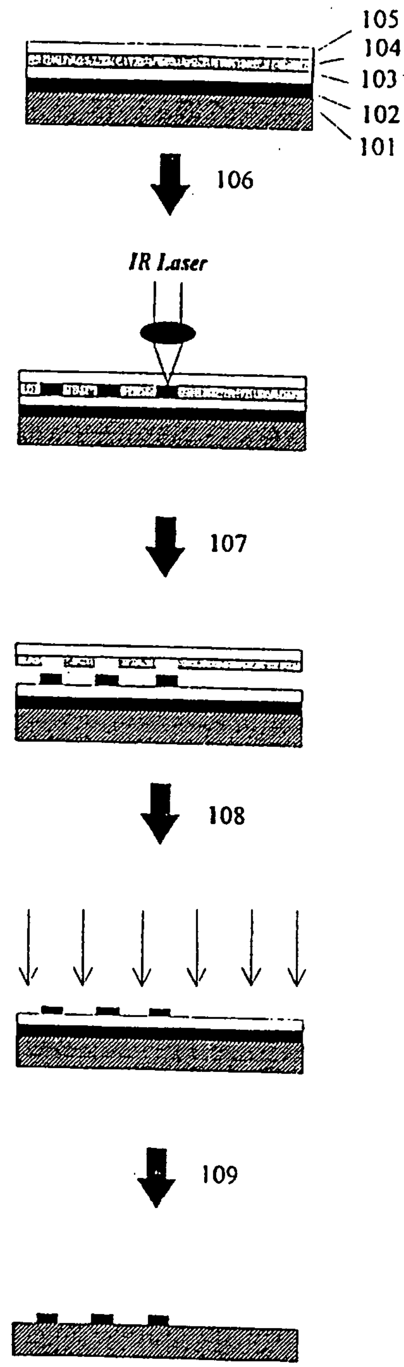

Figure 1 : The structure and image processing steps of the TAT wet plate

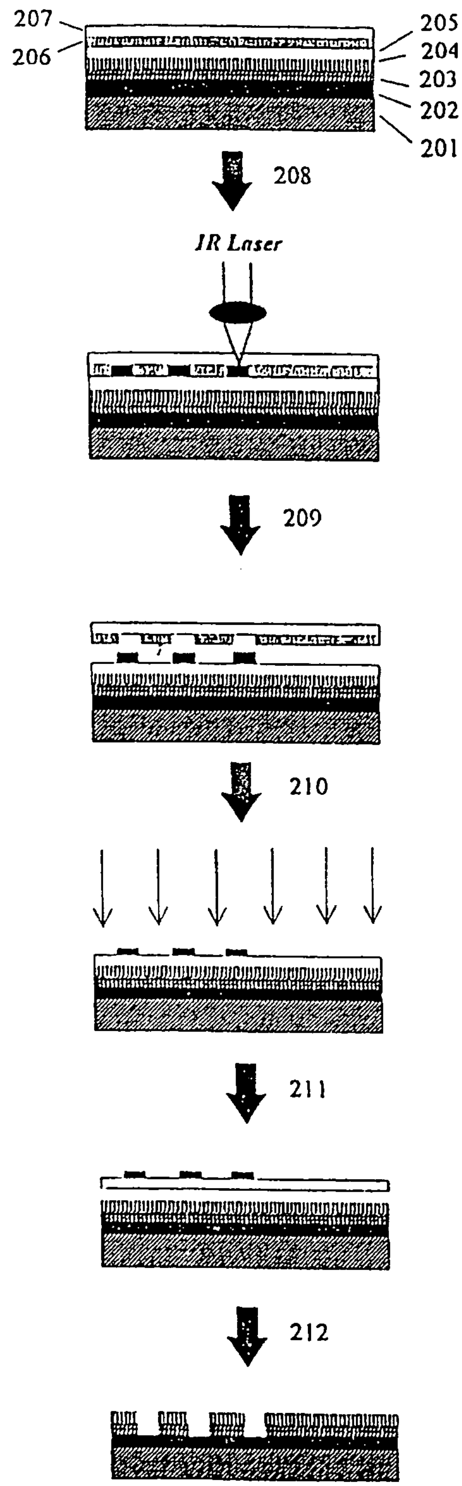

Figure 2 : The structure and image processing steps of the TAT waterless plate

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/07146

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :G03F 1/10, 1/16, 7/075, 7/30, 7/34
US CL :430/5, 201, 253, 272.1, 273.1, 302, 303, 327, 964
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 430/5, 201, 253, 272.1, 273.1, 302, 303, 327, 964

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,342,820 A (KINASHI ET AL) 03 August 1982.	1-17
A	US 5,156,938 A (FOLEY ET AL) 20 October 1992.	1-17
A	US 5,256,506 A(ELLIS ET AL) 26 October 1993.	1-17
X --- Y	US 5,262,275 A (FAN) 16 November 1993, see column 2, lines 13-45.	7-9 ---- 1-17
X	US 5,278,023 A (BILLS ET AL) 11 January 1994, see column 15, lines 30-60; column 16, lines 30-67.	7, 9
X	US 5,506,086 A (VAN ZOEREN) 09 APRIL 1996, see column 2, lines 47-60.	7-9

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents:

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
11 AUGUST 1997	19 SEP 1997

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Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/07146

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P ---- Y,P	US 5,607,814 A (FAN ET AL) 04 March 1997, see column 2, lines 5-35.	1-4, 6, 10, 12-16 ------ 1-17